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PROCESS FOR PREPARING NITRILE COMPOUNDS FROM  
ETHYLENICALLY UNSATURATED COMPOUNDS

The present invention relates to a process for  
5 hydrocyanating an ethylenically unsaturated organic  
compounds to compounds containing at least one nitrile  
function.

It relates more particularly to the hydrocyanation of  
10 diolefins such as butadiene or of substituted olefins  
such as alkenenitriles, for instance pentenenitriles.

French Patent No. 1 599 761 describes a process for  
preparing nitriles by addition of hydrocyanic acid with  
15 organic compounds having at least one ethylenic double  
bond, in the presence of a nickel catalyst and of a  
triaryl phosphite. This reaction can be carried out in  
the presence or absence of a solvent.

20 When a solvent is used in this process of the prior  
art, it is preferably a hydrocarbon, such as benzene or  
xylenes, or a nitrile such as acetonitrile.

The catalyst used is an organic complex of nickel,  
25 containing ligands such as phosphines, arsines,  
stibines, phosphites, arsenites or antimonites.

The presence of a promoter for activating the  
catalysts, such as a boron compound or metal salt,  
30 generally a Lewis acid, is also recommended in said  
patent.

Patent FR-A-2 338 253 has proposed carrying out the  
hydrocyanation of compounds having at least one  
35 ethylenic unsaturation in the presence of an aqueous  
solution of a compound of a transition metal, in  
particular nickel, palladium or iron, and of a  
sulphonated phosphine.

The sulphonated phosphines described in that patent are sulphonated triarylphosphines, and more particularly sulphonated triphenylphosphines.

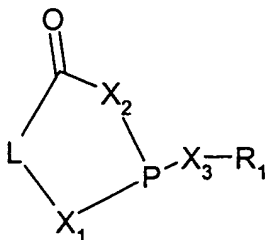
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This process allows correct hydrocyanation, in particular of butadiene and of pentenenitriles, and easy separation of the catalytic solution, by simple settling out, and consequently avoids as much as possible the discharge of effluents or of waste containing the metals used as catalyst.

Research has, however, been carried out in order to find new catalytic systems which give greater performance in terms of catalytic activity and of stability.

One of the aims of the present invention is to propose a new family of ligands which, with the transition metals, make it possible to obtain catalytic systems exhibiting improved activity compared with the known systems.

To this effect, the present invention proposes a process for hydrocyanating a hydrocarbon-based compound containing at least one ethylenic unsaturation by reaction in a liquid medium with hydrogen cyanide in the presence of a catalyst comprising a metallic element chosen from transition metals and an organophosphorus ligand, characterized in that the organophosphorus ligand corresponds to general formula (I) below:



in which:

- $X_1$  and  $X_2$ , which may be identical or different, represent an oxygen atom or the divalent radical NR<sub>2</sub>, in which R<sub>2</sub> represents a hydrogen atom or an alkyl, aryl, sulphonyl, cycloalkyl or carbonyl radical,
  - $X_3$  represents a covalent bond, an oxygen atom or the divalent radical NR<sub>2</sub>, in which R<sub>2</sub> represents a hydrogen atom or an alkyl, aryl, sulphonyl, cycloalkyl or carbonyl radical,
  - the radical R<sub>1</sub> represents a linear or branched alkyl radical having from 1 to 12 carbon atoms that may contain hetero atoms, or a substituted or unsubstituted aromatic or cycloaliphatic radical that may contain hetero atoms or one or more rings in fused or nonfused form,
  - L represents a linear or branched divalent alkyl radical having from 1 to 12 carbon atoms that may contain hetero atoms, or a substituted or unsubstituted aromatic or cycloaliphatic divalent radical that may contain hetero atoms and one or more rings in fused or nonfused form.
- 25 In a preferred embodiment,  $X_1$  and  $X_2$  are different and represent equally an oxygen atom or a divalent radical NR<sub>2</sub>.

30 Preferably, the bonds of the divalent radical are in the ortho-position in the case of an aromatic radical or carried by the same carbon or two carbons in the alpha-position with respect to one another in the case of an acyclic or cyclic alkyl radical.

35 Moreover, in a preferred embodiment of the invention  $X_3$  represents oxygen.

In addition, L advantageously represents:

\* a derivative of salicylamide, optionally

functionalized on the aromatic ring, and/or by formation of the aliphatic or aromatic secondary amide, for instance salicylanilide or naphtol AS.

- 5 \* a derivative of anthranilic acid, substituted on the aromatic ring, and/or by formation of the aliphatic or aromatic secondary amine, for instance N-phenylanthranilic acid or N-methyl anthranilic acid,  
\* an alpha amino acid, more preferably a natural amino acid derivative in which the nitrogen atom is  
10 monosubstituted with an aliphatic, aromatic, aryl sulphonyl or carbonyl group.

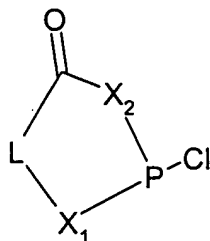
These compounds can be obtained by reacting, in the presence of a base, a compound A of formula (II) below:

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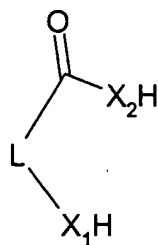
with an appropriate halophosphorus, more particularly chlorophosphorus, derivative of formula (III) below:

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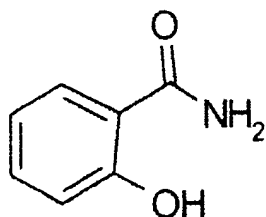
The halophosphorus derivative can be obtained by reacting PCl<sub>3</sub> with a compound of formula (IV) below:

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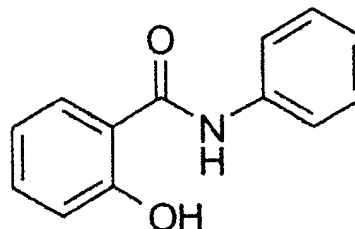


Such structures of formula (IV) that are preferred can correspond to the compounds below:

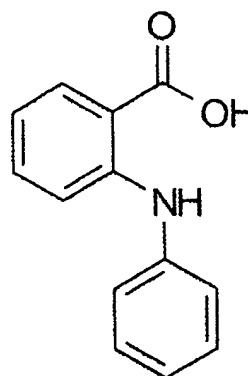
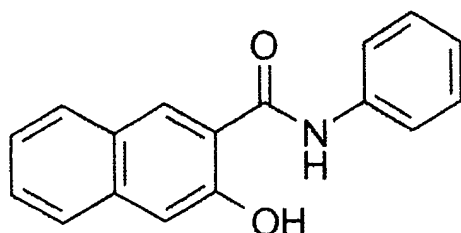
salicylamide



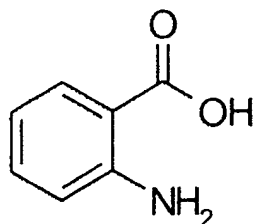
salicylanilide



Naphtol AS



anthranilic acid



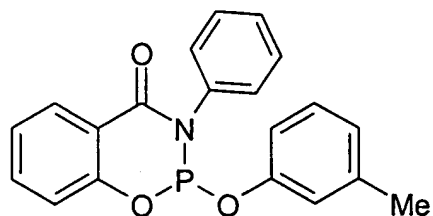
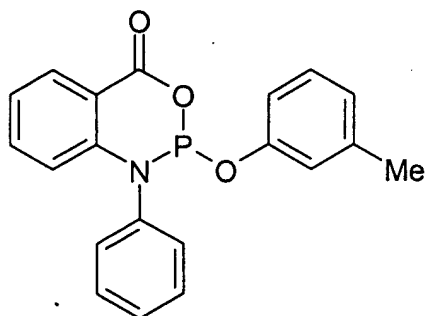
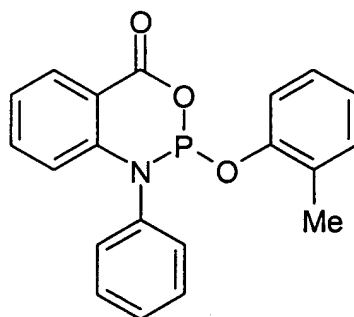
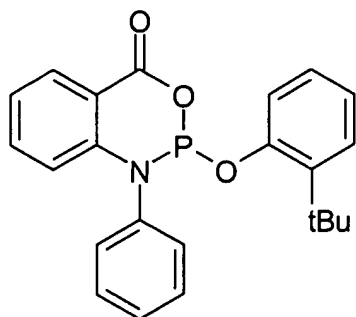
N-phenylanthranilic acid

The compounds of formula (I) can be obtained by means of other processes, in particular when X<sub>3</sub> represents a covalent bond.

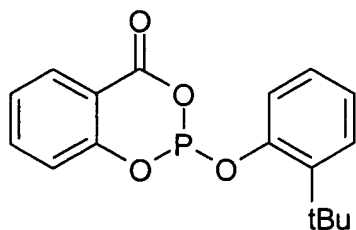
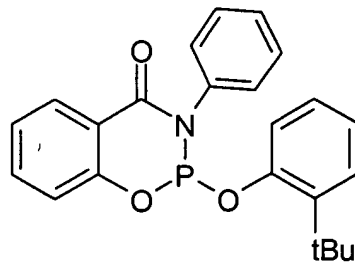
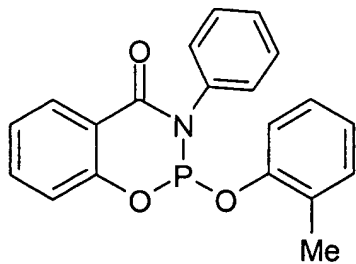
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By way of examples of compounds of general formula I, mention may be made of the compounds listed below (in the following formulae, the symbol Me signifies the methyl radical, and the symbol tBu signifies the tert-butyl radical):

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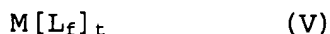
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According to a preferred characteristic of the invention, the metal element is chosen from the group comprising nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium and mercury. Among these metals, nickel is the preferred metal.

According to the invention, the catalyst advantageously corresponds to general formula (V):



5 in which:

M is a transition metal,

$L_f$  represents the organophosphorus ligand of formula (I) and t represents a number between 1 and 6 (limits inclusive).

10

The organometallic complexes containing the compounds of formula (I) can be prepared by bringing a solution of a compound of the metal selected into contact with a solution of a compound of formula (I).

15

The compound of the metal can be dissolved in a solvent.

20 In the compound used, the metal may be in the oxidation state that it will have in the organometallic complex, or in a higher oxidation state.

25 By way of example, it may be indicated that, in the organometallic complexes of the invention, rhodium is in oxidation state (I), ruthenium in oxidation state (II), platinum in oxidation state (0), palladium in oxidation state (0), osmium in oxidation state (II), iridium in oxidation state (I), and nickel in oxidation state (0).

30

If, during the preparation of the organometallic complex, the metal is used in a higher oxidation state, it may be reduced in situ.

35 The organometallic complexes comprising the compounds of formula (I) can be used as catalysts in olefin hydrocyanation reactions or the hydrocyanation of unsaturated compounds containing, for example, a nitrile function.

As transition metal, use is preferably made of the compounds of transition metals, more particularly the compounds of nickel, of palladium, of iron or of  
5 copper.

Among the abovementioned compounds, the most preferred compounds are those of nickel.

10 By way of non-limiting examples, mention may be made of:

- compounds in which nickel is in oxidation state zero, such as potassium tetracyanonickelate  
15  $K_4[Ni(CN)_4]$ , bis(acrylonitrile)nickel zero, bis(cycloocta-1,5-diene)nickel (also called  $Ni(cod)_2$ ) and derivatives containing ligands, such as tetrakis(triphenylphosphine)nickel zero;
- 20 - compounds of nickel such as carboxylates (in particular acetate), carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite, phosphate and derivatives, iodide,  
25 nitrate, sulphate, sulphite, aryl- and alkylsulphonates.

When the nickel compound used corresponds to a nickel oxidation state greater than zero, a nickel-reducing  
30 agent that reacts preferentially with the nickel under the reaction conditions is added to the reaction medium. This reducing agent may be organic or inorganic. As non-limiting examples, mention may be made of borohydrides such as  $BH_4Na$  or  $BH_4K$ , Zn powder,  
35 magnesium or hydrogen.

When the nickel compound used corresponds to the zero oxidation state of nickel, it is also possible to add a reducing agent of the abovementioned type, but such



addition is not mandatory.

When an iron compound is used, the same reducing agents are suitable.

5

In the case of palladium the reducing agents may, in addition, be elements of the reaction medium (phosphine, solvent, olefin).

10 The organic compounds containing at least one ethylenic double bond that are more particularly used in the present process are diolefins such as butadiene, isoprene, hexa-1,5-diene, cycloocta-1,5-diene, ethylenically unsaturated aliphatic nitriles, 15 particularly linear pentenenitriles such as 3-pentene-nitrile or 4-pentenenitrile, monoolefins such as styrene, methylstyrene, vinylnaphthalene, cyclohexene, methylcyclohexene, and mixtures of several of these compounds.

20

The pentenenitriles in particular may contain amounts, generally minor amounts, of other compounds, such as 2-methyl-3-butenenitrile, 2-methyl-2-butenenitrile, 2-pentenenitrile, valeronitrile, adiponitrile, 25 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating, for example, from the prior hydrocyanation reaction of the butadiene to unsaturated nitriles.

30 The reason for this is that the hydrocyanation of butadiene is accompanied by the formation, along with the linear pentenenitriles, of not insignificant amounts of 2-methyl-3-butenenitrile and 2-methyl-2-butenenitrile.

35

The catalyst system used for the hydrocyanation according to the process of the invention may be prepared before it is introduced into the reaction zone, for example by adding the appropriate amount of

selected transition metal compound and, optionally, of reducing agent to the compound of formula (I), alone or dissolved in a solvent. It is also possible to prepare the catalyst system "in situ" by simply adding the compound of formula (I) and the transition metal compound to the hydrocyanation reaction medium before or after adding the compound to be hydrocyanated.

The amount of compound of nickel or of another transition metal used is chosen so as to give a concentration, in moles of transition metal per mole of organic compounds to be hydrocyanated or isomerized, of between  $10^{-4}$  and 1, preferably of between 0.005 and 0.5 mol of nickel or of the other transition metal used.

The amount of compound of formula (I) used to form the catalyst is chosen such that the number of moles of this compound, relative to 1 mol of transition metal, is from 0.5 to 500, and preferably from 2 to 100.

Although the reaction is generally carried out without solvent, it may be advantageous to add an inert organic solvent. The solvent may be a solvent for the catalyst which is miscible with the phase comprising the compound to be hydrocyanated, at the hydrocyanation temperature. By way of examples of such solvents, mention may be made of aromatic, aliphatic or cycloaliphatic hydrocarbons.

The hydrocyanation reaction is generally carried out at a temperature of  $10^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ , and preferably of  $30^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ . It may be carried out in a single-phase or in a two-phase medium.

The process of the invention may be carried out continuously or batchwise.

The hydrogen cyanide used may be prepared from metal

cyanides, in particular sodium cyanide, or from cyanohydrins, such as acetone cyanohydrin, or by any other known synthesis process.

- 5 The hydrogen cyanide is introduced into the reactor in gaseous form or in liquid form. It may also be dissolved beforehand in an organic solvent.

10 In the context of a batchwise implementation, it is possible in practice to charge a reactor, purged beforehand by means of an inert gas (such as nitrogen or argon), either with a solution containing all or a part of the various constituents, such as the compound to be hydrocyanated, the compounds of formula (I), the  
15 transition metal compound, the optional reducing agent and solvent, or with said constituents separately. Generally, the reactor is then taken to the selected temperature. The hydrogen cyanide is then itself introduced, preferably continuously and regularly.

20 When the reaction (whose development can be monitored by assaying samples) is at an end, the reaction mixture is withdrawn, after cooling, and the reaction products are isolated, by distillation for example.

25 An enhancement of the process for hydrocyanating ethylenically unsaturated compounds according to the present invention relates in particular to the hydrocyanation of said ethylenically unsaturated  
30 nitrile compounds by reaction with hydrogen cyanide and consists in using a catalyst system in accordance with the present invention with a cocatalyst consisting of at least one Lewis acid.

35 The ethylenically unsaturated compounds that may be used in this enhancement are in general those that were mentioned for the basic process. However, it is more particularly advantageous to apply it to the reaction consisting of hydrocyanation of ethylenically

unsaturated aliphatic nitriles to dinitriles, in particular apply it to the linear pentenenitriles such as 3-pentenenitrile or 4-pentenenitrile, and mixtures thereof.

5

These pentenenitriles may contain amounts, generally minor amounts, of other compounds, such as 2-methyl-3-butenitrile, 2-methyl-2-butenitrile, 2-pentenenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating from the prior hydrocyanation reaction of the butadiene and/or from the isomerization of 2-methyl-3-butenitrile to pentenenitriles.

15 The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of ethylenically unsaturated aliphatic nitriles, to improve the linearity of the dinitriles obtained, i.e. the percentage of linear dinitriles relative to the total dinitriles formed, and/or to increase the activity and service life of the catalyst.

In the present text, the term "Lewis acid" is intended to mean, according to the usual definition, compounds that accept electron pairs.

Use may in particular be made of the Lewis acids mentioned in the work edited by G.A. Olah, "Friedel-Crafts and related Reactions", volume I, pages 191 to 197 (1963).

The Lewis acids that may be used as cocatalysts in the present process are chosen from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of Elements. These compounds are most often salts, especially halides, such as chlorides or bromides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkylsulphonates, especially fluoroalkylsulphonates or

perfluoroalkylsulphonates, haloalkylacetates, perhaloalkylacetates, carboxylates and phosphates.

By way of non-limiting examples of such Lewis acids, mention may be made of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium trifluoromethylsulphonate, indium trifluoromethyl acetate, the chlorides or bromides of rare earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thallium, ytterbium and lutetium, and cobalt chloride, ferrous chloride and yttrium chloride.

As a Lewis acid it is also possible to use organometallic compounds such as triphenylborane or titanium isopropoxide.

Mixtures of several Lewis acids can of course be used.

Among Lewis acids, zinc chloride, zinc bromide, stannous chloride, stannous bromide, triphenylborane, and zinc chloride/stannous chloride mixtures are most particularly preferred.

The Lewis acid cocatalyst used generally represents from 0.01 to 50 mol per mole of transition metal compound, more particularly of nickel compound, and preferably from 1 to 10 mol per mole.

As for the implementation of the basic process of the invention, the catalyst solution used for the hydrocyanation in the presence of Lewis acid may be prepared prior to its introduction into the reaction zone, or in situ, for example by adding the various components of the catalyst system to the reaction medium.

It is also possible, under the conditions of the hydrocyanation process of the present invention, and in particular by working in the presence of the above-described catalyst comprising at least one compound of formula (I) and at least one transition metal compound, to carry out the isomerization of 2-methyl-3-butenitrile to pentenenitriles, and more generally of branched unsaturated nitriles to linear unsaturated nitriles, in the absence of hydrogen cyanide.

The 2-methyl-3-butenitrile subjected to the isomerization according to the invention may be used alone or as a mixture with other compounds.

Thus 2-methyl-3-butenitrile may be deployed as a mixture with 2-methyl-2-butenitrile, 4-pentenitrile, 3-pentenitrile, 2-pentenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

It is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of butadiene with HCN in the presence of at least one compound of formula (I) and of at least one transition metal compound, more preferably of a compound of nickel in oxidation state 0, as defined above.

In the context of this preferred variant, since the catalyst is already present for the butadiene hydrocyanation reaction, it is sufficient to stop any introduction of hydrogen cyanide in order to allow the isomerization reaction to take place.

It is possible, where appropriate, in this variant to effect a gentle purging of the reactor by means of an inert gas, such as nitrogen or argon for example, in order to expel the hydrocyanic acid which might still be present.

The isomerization reaction is generally carried out at a temperature of 10°C to 200°C, and preferably of 60°C to 180°C.

5

In the preferred case of an isomerization immediately following the butadiene hydrocyanation reaction it will be advantageous to operate at the temperature at which the hydrocyanation was carried out.

10

As for the process for hydrocyanating ethylenically unsaturated compounds, the catalyst system used for the isomerization may be either already present in the medium or may be prepared according to the preparation methods already described above.

15

Although the isomerization reaction is generally carried out without solvent, it may be advantageous to add an inert organic solvent, which may be that of the subsequent extraction. This is in particular the case when such a solvent has been used in the butadiene hydrocyanation reaction that served to prepare the medium subjected to the isomerization reaction. Such solvents can be chosen from those that were mentioned above for the hydrocyanation.

25

However, the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out using a catalyst system in accordance with the invention for the above steps of formation of unsaturated nitriles and the above isomerization step, it being possible for the reaction consisting of hydrocyanation of unsaturated nitriles to dinitriles to be carried out with a catalyst system in accordance with the invention or any other catalyst system already known for this reaction.

30

35

Similarly the reaction consisting of hydrocyanation of the olefin to unsaturated nitriles and the

isomerization thereof may be carried out with a catalyst system that is different from that of the invention, the step consisting of hydrocyanation of unsaturated nitriles to dinitriles being carried out  
5 with a catalyst system in accordance with the invention.

The following examples illustrate the invention.

10 In the examples, the abbreviations used have the meanings indicated below.

cod: 1,5-cyclooctadiene

eq: equivalent

3PN: 3-pentenenitrile

15 4PN: 4-pentenenitrile

3+4PN: 3PN + 4PN

DC(Y): degree of conversion of the product to be hydrocyanated, Y, corresponding to the ratio of the number of moles of Y converted to the initial number of  
20 moles of Y

Linearity (L): ratio of the number of moles of adiponitrile (AdN) formed to the number of moles of dinitriles formed (sum of the moles of AdN, ethylsuccinonitrile (ESN) and methylglutaronitrile  
25 (MGN))

GC: gas chromatography

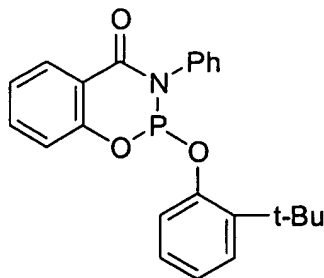
ml: millilitre

mol: mole(s)

mmol: millimole(s).

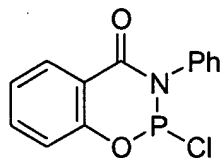
30 Ph: phenyl

Example 1: Synthesis of ligand A of formula below





For the preparation of ligand A, starting materials that are used are ortho-t-butylphenol and a phosphorochloridite for which the preparation process is described in an article by R.A. Sabirova, L.V. Nesterov, A.E. Arbuzov, published in *Zh. Obshch. Khim.* 1967, 37, 732-4, of formula below:



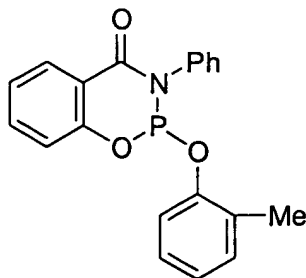
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The procedure for preparing ligand A is as follows:

1.1 g of phosphorochloridite of formula above are dissolved in 5 ml of anhydrous tetrahydrofuran and 10 ml of anhydrous toluene, under argon, in a 100 ml round-bottomed flask. The solution is stirred at -10°C. The dropping funnel is charged with a solution of 600 mg of ortho-t-butylphenol and of 0.85 ml of triethylamine in 2 ml of anhydrous tetrahydrofuran, and this solution is introduced dropwise into the reaction medium maintained at -10°C: a white precipitate forms. The suspension is vigorously stirred for 18 h at 25°C and then filtered, under argon, on a bed of basic alumina I. After rinsing with toluene, the filtrate is concentrated under reduced pressure, to give 1.25 g of crude product in the form of a thick translucent oil. NMR analysis confirms the identity of the product obtained corresponding to the formula above.

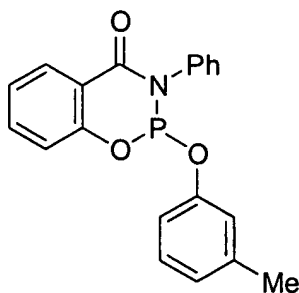
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Example 2: Synthesis of a ligand B of formula below



This ligand is prepared according to the same procedure as ligand A, using ortho-cresol. 1.67 g of the phosphorochloridite and 0.65 g of ortho-cresol giving, under these conditions, 1.27 g of product corresponding to the formula above.

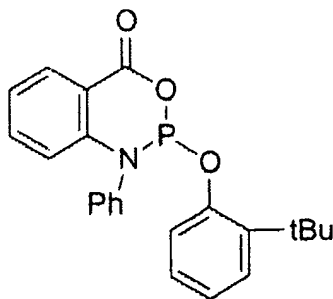
Example 3: Synthesis of a ligand C of formula below



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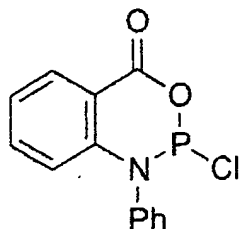
This ligand is prepared according to the same procedure as ligand A, using meta-cresol: 1.67 g of the phosphorochloridite and 0.65 g of meta-cresol giving, under these conditions, 1.57 g of the product corresponding to the formula above.

Example 4: Synthesis of a ligand D of formula below



20

This ligand is obtained by reaction of ortho-tert-butylphenyl with a phosphorochloridite of formula below:



This phosphorochloridite is prepared according to the following procedure:

5 15 ml of  $\text{PCl}_3$  are added to 10.7 g of *N*-phenyl-anthranilic acid, followed by 20 ml of anhydrous toluene, under argon, in a 100 ml round-bottomed flask. The thick suspension thus obtained is stirred for 1 h at  $25^\circ\text{C}$  and then gradually brought to  $60^\circ\text{C}$  and,  
10 finally, refluxed for 3 h. The solution thus obtained is cooled to ambient temperature, filtered under an inert atmosphere and concentrated under reduced pressure. A red solid is obtained, which is purified by trituration in pentane and then filtration under an  
15 inert atmosphere. 12.5 g of a red solid approximately 85% pure are recovered.

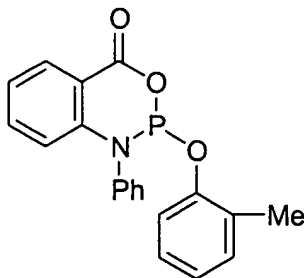
The procedure for preparing ligand D is as follows:

1.1 g of the phosphorochloridite of formula above are  
20 dissolved in 5 ml of anhydrous tetrahydrofuran and 10 ml of anhydrous toluene, under argon, in a 100 ml round-bottomed flask. The solution is stirred at  $-10^\circ\text{C}$ . The dropping funnel is charged with a solution of 600 mg of *ortho*-*t*-butylphenol and of 0.85 ml of  
25 triethylamine in 2 ml of anhydrous tetrahydrofuran, and this solution is introduced dropwise into the reaction medium maintained at  $10^\circ\text{C}$ : the initially red solution loses its colour, and a yellow precipitate forms. The suspension is stirred vigorously for 18 h at  $25^\circ\text{C}$  and  
30 filtered, under argon, on a bed of basic alumina I. After rinsing with toluene, the filtrate is concentrated under reduced pressure, to give 1.3 g of crude product in the form of a thick translucent oil.

NMR analysis confirms the identity of the product obtained corresponding to the formula above.

Example 5: Synthesis of a ligand E of formula below

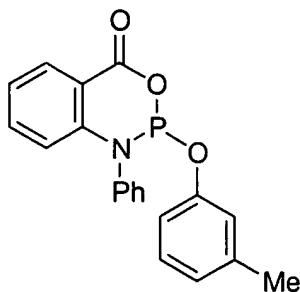
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This ligand is prepared according to the same procedure as ligand D, using ortho-cresol: 1.67 g of the  
10 phosphorochloridite and 0.65 g of ortho-cresol giving, under these conditions, 1.56 g of the product corresponding to the formula above.

Example 6: Synthesis of a ligand F of formula below

15



This ligand is prepared according to the same procedure as ligand D, using meta-cresol: 1.67 g of the  
20 phosphorochloridite and 0.65 g of meta-cresol give, under these conditions, 1.57 g of the product corresponding to the formula above.

Example 7: Hydrocyanation of 3-pentenenitrile (3PN) to adiponitrile (AdN).

25

A 60 ml Shott-type glass tube equipped with a septum stopper is successively charged, under an argon atmosphere, with:

- the ligand (2.5 eq),
- 5        - 1.21 g (15 mmol; 30 eq) of anhydrous 3PN,
- 138 mg (0.5 mmol; 1 eq) of  $\text{Ni}(\text{cod})_2$ , and
- 68 mg (0.5 mmol; 1 eq) of zinc(II) chloride.

The mixture is brought to 70°C with stirring. Acetone  
10 cyanohydrin is injected into the reaction medium by means of a syringe pump at a flow rate of 0.45 ml per hour. After injection for 3 hours, the syringe pump is stopped. The mixture is cooled to ambient temperature, diluted with acetone, and analysed by gas  
15 chromatography.

Under these conditions, the following results are obtained:

<i>Ligand</i>	<i>DC(3PN)</i>	<i>Linearity</i>
<b>A</b>	36%	44%
<b>B</b>	12%	34%
<b>C</b>	24%	74%
<b>D</b>	32%	53%
<b>E</b>	10%	72%
<b>F</b>	8%	69%